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13. ABSTRACT *(Maximum 200 words)*

The grant was initiated on May 1 5,1998 and was completed in August 2001. We have explored the compositions at which in-situ toughened ct-SiAION can be obtained. This essentially encompasses the entire single a-phase region. It includes both rare-earth ion-added compositions and alkali/alkali-earth ion-added compositions. We have made a systematic effort to obtain kinetic data on phase transformation at different compositions, since this knowledge is critically important for the precise control of nucleation and growth, which dictate the microstructure. We have developed methods for controlling microstructure in ci-SiAION prepared from commercial a-Si3N4 powders. These materials have faster transformation rate and the microstructure control must rely on nucleation treatment of external seeding. We have developed the method to grow and harvest seed crystals, of a controlled composition, size and morphology, which can be used to nucleate a'-SiAION grains in the ceramic to allow tailored grain growth. We have developed a theory for grain growth, based on the recent observations of the morphology of isolated grains from the oxynitride liquid. This model successfully predicted the novel shape transition observed experimentally. We have developed a wet chemical technique for etching the highly stable a'-SiAION, which until now has proved difficult for ceraniographic preparation. We have shown that the mechanical strength of ct-SiAION can exceed I CPa and the strength retention is good at least up to 1350 0C. We have obtained R-curves for a'SiAION ccramics, and show that they can reach a toughness of 11-12 MPa m1t which compares favorably with the state-of-the-au j3 silicon nitride.

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I. TITLE OF PROJECT

AASERT STUDENT RESEARCH ON IN-SITU TOUGHENED α'-SIALON

TECHNICAL AND FINAL REPORT

AUGUST 15, 1998-AUGUST 31, 2001

U.S. AIR FORCE GRANT NO. F49620-98-1-0470

PRINCIPAL INVESTIGATOR

I-WEI CHEN

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA

II. OBJECTIVES

The objective of this research is to design experiments to expedite the development and understanding of the large family of in-situ toughened α'-SiAlON that has been recently invented. The underlying premise is that the very large degree of freedom in alloy design for α'-SiAlON, which encompasses a broad range of composition and processing conditions, can be advantageously focussed by utilizing principles of physical chemistry and statistical design that identify unbiased experimental conditions and facilitate the determination of the cause-effect relations. The subjects to be investigated include the role of interstitial cations (alkali-earth and rare earth), regions of phase field, processing temperature and time, and characteristics of starting powders in the densification, microstructure development and resulting strength and fracture toughness of these ceramics

III. STATUS OF EFFORT

The grant was initiated on May 15, 1998 and was completed in August 2001. We have explored the compositions at which in-situ toughened α'-SiAlON can be obtained. This essentially encompasses the entire single α'-phase region. It includes both rare-earth ion-added compositions and alkali/alkali-earth ion-added compositions. We have made a systematic effort to obtain kinetic data on phase transformation at different compositions, since this knowledge is critically important for the precise control of nucleation and growth which dictate the microstructure. We have developed methods for controlling microstructure in α'-SiAlON prepared from commercial α-Si_3N_4 powders. These materials have faster transformation rate and the microstructure control must rely on nucleation treatment of external seeding. We have developed the method to grow and harvest seed crystals, of a controlled composition, size and morphology, which can be used to nucleate α'-SiAlON grains in the ceramic to allow tailored grain growth. We have developed a theory for grain growth, based on the recent observations of the morphology of isolated grains from the oxynitride liquid. This model successfully predicted the novel shape transition observed experimentally. We have developed a wet chemical technique for etching the highly stable α'-SiAlON, which until now has proved difficult for ceramographic preparation. We have shown that the mechanical strength of α'-SiAlON can exceed 1 GPa and the strength retention is good at least up to 1350 °C. We have obtained R-curves for α'-SiAlON ceramics, and show that they can reach a toughness of 11-12 MPa $m^{1/2}$, which compares favorably with the state-of-the-art β silicon nitride.

IV. ACCOMPLISHMENTS/NEW FINDINGS

<u>*Nucleation Control of Microstructure*</u>

The essence of microstructure control that enables the formation of in-situ toughened a'-SiAlON is to control nucleation of α' phase so that relatively few nuclei compete for growth. There are three general ways to achieve this goal. First, starting powders can be chosen to be energetically more stable or crystallographically less similar to the product phase. This implies that β- Si_3N_4 powders are better as the starting powders. The second method is to choose a composition with less stability for

the α' phase. This dictates the choice of larger cations or compositions near the phase boundary. An extension of the second approach is to take advantage the temperature dependence of the phase stability. This dictates the use of lower temperature for nucleation or use different heating rates to manipulate nucleation and growth. We have demonstrated that these three approaches, individually or in combination, with various conceivable variations, can be practiced to render any single phase α'-SiAlON composition amenable to obtaining a fibrous microstructure.

We have found that for highly stable single phase α'-SiAlON compositions the above approaches are more difficult to practice because the driving force is too large and nucleation rate too fast. In such a case, we have introduced seed crystals of single phase α'-SiAlON composition to predetermine the nucleation statistics. This approach has proved successful. As a result, we are now able to obtain high toughness single phase α'-SiAlON ceramics of any composition using either α or β-Si_3N_4 powders.

A parallel effort has been made to prepare α'-SiAlON seeds of an appropriate size and shape. It is noted that, to be effective, seeds must have the same composition of the final phase, or have a composition that is thermodynamically more stable. This is a difficult task compared with the other seeding efforts reported in the literature, where the seeding can be provided simply by using compounds of an appropriate phase, e.g. β-Si_3N_4 or α SiC. In our case, such compounds invariably dissolve, so the seeds need to have a composition that is stable, i.e., it should be an α-Si_3N_4 solid solution itself. This task has been successful and a method for obtaining high-yield seed crystals of a variety size, shape and compositions have been developed. The physical chemistry of seed formation and growth has been investigated. In particular, the effect of different dopant cations has been determined.

Our research on α'-SiAlON has also systematically explored the difference between compositions involving (a) rare earth cations of different sizes and (b) alkali and alkali earth cations, primarily Li and Ca. The stability of the single phase α'-SiAlON varies significantly and this has a major impact on the phase nucleation and microstructural development of the ceramics. In addition, the kinetics are influenced by the different liquid viscosity due to the presence of different cations as well as the different interface characteristics due to the segregation of dopants. By controlling these factors separately, it is now possible to obtain the desired microstructure for all the rare-earth cation α'-SiAlON and for Ca-α'-SiAlON.

Mechanical Properties of α-SiAlON

We have investigated the mechanical properties of α-SiAlON using three methods. Preliminary hardness and toughness data were obtained using the indentation method. Although toughness is usually underestimated by this method, the systematic trend between ceramics of different compositions and different microstructures is usually preserved. A more systematic investigation has been made using R-curve measurements. This was performed in-situ under a microscope in the four-point bending configuration. The R-curves show a very strong correlation with the microstructure and are sensitive to the compositions. The values at small crack

extension, approximately 50-100 μm, appear to correspond well to the values of indentation toughness. Very high toughness of 11-12 MPa $m^{1/2}$ is seen in some microstructures, which compares favorably with the toughness of in-situ toughened β-silicon nitride. This method is particularly powerful in evaluating the influence of seeding and heat treatment on the mechanical properties. Finally, three-point bending has been performed to obtain strength data at room temperature and elevated temperatures, up to 1350 °C. Strength values exceeding 1 GPa have been obtained in some ceramics, which can be retained (up to 70%) at high temperatures. Optimization of the strength-toughness combination seems possible and has been attempted by using minor dopants and heat treatment. Further major progress in this area is anticipated in the next few years based on our preliminary findings.

Thermodynamics of Anisotropic Si_3N_4 Crystals

The recent observation of Wang, Tien and Chen on β- Si_3N_4 showed that an elongated rod grown from the liquid can have a concave end. Such morphology implies that material transport must come from the corner, and it in turns implies long range diffusion along the side surface or in a boundary layer near the side surface. Interface control is obviously an important factor in directing growth anisotropy. We have developed a thermodynamic theory for the chemical potential of surface atoms of an anisotropic crystal, with and without facet, under equilibrium and non-equilibrium conditions. The equilibrium shape has been obtained, and criterion for shape evolution has also been formulated. Using this theory, the evolution of the aspect ratio of grains during phase transformation and Ostwald ripening can now be understood. In addition, the case of interface control can also be rigorously treated with respect to the underlying equilibrium conditions to account for different growth scenarios. This theory has been extended to silicon carbide as well. Further experimental effort to determine the growth kinetics and the shape evolution has been made and the results have revealed the importance of compositional evolution during the precipitation and ripening process.

Microstructure Determination of α'-SiAlON

We have developed a new chemical etching technique that reveals the microstructure clearly under a light microscope. The new technique takes advantage of the bonding difference between nitride and oxide to differentially dissociate the Si-O-Si bond and the Si-N-Si bond. Alternatively, the nitrogen bond can be converted to oxygen bond resulting in a large change in refractive index. This technique makes it feasible to perform quantitative microscopy using image analysis softwares.

A new development in quantifying the microstructure of anisotropic grains has been made. Such microstructure must rely upon information on two-dimensional cross sections. Previous methods measured rectangular shapes on such cross sections; the statistics of such shapes are compared, using reverse transformation, with postulated three-dimensional shape statistics. We have shown that a linear intercept method works equally well for self-similar shapes. The advantage to the linear intercept method is that it is much faster for data collection, and it has much better sampling statistics.

(j) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "R-Curve Behavior of In-situ Toughened a-SiAlON Ceramics," J. Am. Ceram. Soc., 84 [4] 884-86 (2001).

(k) M. Zenotchkine, 'R. Shuba, J-S. Kim and I-Wei Chen, "Synthesis of α-SIALON Seed Crystals," J. Am. Ceram. Soc., 84 [7] 1651-53 (2001).

(l) I-W. Chen and R. Shuba, "Structure and Property of SiAlON Ceramics", to appear in Encyclopedia of Materials: Science and Technology, ed. K.H.J. Baschow, R.W. Cahn, M.C. Flemings, B. Ilschner, E.J. Kramer and S. Mahajan, Elsevier Science Ltd. Oxford, UK (2001).

(m) A. Pechenik and I-W. Chen, "Advanced Silicon Nitride Ceramics", Advanced Materials and Processing, p. 37, March (2001).

VII. INVITED TALKS BY PI

(a) "Innovations in Processing of Structural Ceramics with High Aspect Ratio Features," International Symposium on Novel Synthesis and Processing of Ceramics, Kurume, Japan, October 1997.

(b) "Paradigms of Innovations in Materials Research," plenary lecture, Annual Meeting of the Chinese Society for Materials Science, Tainan, Taiwan, Novemeber 1997.

(c) "Phase Relations and Phase Stability in SiAlON Systems," Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 1998.

(d) "Silicon Nitride at sub 1400 °C--Issues and Possible Solutions," Workshop on Ultra High Temperature Ceramics, May 1998, Boulder, CO, May 1998.

(e) "Silicon Nitride -- A Matter of Kinetics," Conference on New Developments in High Temperature Ceramics, Istanbul, Turkey, August 1998.

(f) "Silicon Nitride and SiAlON," plenary lecture at the First International Conference on Inorganic Materials, Versailles, France, September 1998.

(g) "Innovations in Structural Ceramics and Composites," Brown University, Providence, April 1999.

(h) "Using Silicon Nitride Based Ceramics at High Temperatures," ASME Meeting, Nashville, TN, November 1999.

(i) "In Search of Ceramic Steel," Department of Materials Science and Engineering, University of California-Berkeley, January 2001.

VIII. TRANSITIONS, PATENTS, AND HONORS

Samples of in-situ toughened α'-SiAlON have been provided to a leading US cutting tool manufacturer and a leading German cutting tool manufacturer to evaluate their cutting performance. This evaluation process is on-going as the cutting applications are material specific, depending on the work piece as well as the tool. Thus, composition, microstructure and property optimization is required for each cutting application.

Two patents have been issued by the US Patent Office. (No. 5,908,798, "In-situ Toughened Alpha Prime Sialon Based Ceramics," by I-Wei Chen and Anatoly Rosenflanz; and No. 6,139,791, "Method of Making In-situ Toughened Alpha Prime Sialon Based Ceramics," by I-Wei Chen and Anatoly Rosenflanz.)

Collaborative research with Prof. R. Riedel of Damstadt Technical University of Germany has resulted in the discovery of a new structure of solid solution of Si-Al-O-N. A patent application has been filed with Prof. Chen as a co-inventor.